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Phase transitions in KH₂PO₄ and RbH₂PO₄ to 14 GPa observed by capacitance change in a diamond anvil cell

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Phase transitions in KH_2PO_4 (KDP) and RbH_2PO_4 (RDP) at room temperature for pressures up to 14 GPa have been determined by means of capacitance measurements using a diamond anvil cell. Phase transitions occur in KDP near 2.5 and 7.0 GPa. In RDP, a transition was detected near 5.4 GPa.

I. INTRODUCTION

Much work has been done on pressure effects in ferroelectrics. Pressures up to several GPa were used, with a temperature range between 100–300 K. Potassium dihydrogen phosphate, KH_2PO_4 (KDP) and its alkali phosphate and arsenate isomorphs form an important class of hydrogen bonded ferroelectrics that have been extensively studied,[1-9] especially with respect to their ferroelectric properties. Pressure is an important parameter in these studies. To investigate the dielectric properties in ferroelectric and related crystals at much higher pressure, we have carried out this work in a diamond anvil cell (DAC).

Dielectric anomalies accompany phase transitions, especially ferroelectric phase transitions. The relative dielectric constant ϵ_r can be found from the capacitance C of a parallel-plate capacitor by the formula

$$C = \epsilon_r \epsilon_0 A/d, \tag{1}$$

where ϵ_0 is the MKS constant, and A and d are the plate area and separation.

The capacitance of a sample will change gradually with increasing pressure. At a phase transition, the capacitance will change suddenly. Therefore, we can detect the phase transition in a sample at high pressure by measuring its capacitance.

We carried out experiments based on this idea with our DAC. By means of repeated experiments, we have been the first to observe phase transitions in KDP and RDP in a pressure range extending as high as 14 GPa. These are also the first measurements of capacitance using a DAC. This technique could become an important method for using the DAC to study insulator-insulator transitions at high pressure. It extends DAC investigations into a new area, that of dielectric investigations.

II. EXPERIMENTAL METHOD

The DAC used in this work is a somewhat improved version of the DAC used previously. The design of this previously used DAC provides remarkable advantages[10] over other common DAC types.

Our experimental method consists in measuring capacitance versus pressure, to detect phase transitions evidenced by capacitance anomalies. We used two parallel molybdenum sheets as electrodes of a capacitor, as shown in Fig. 1(a). These Mo electrodes were made by photoetching them away from a base, which is a phenolic methylal glue film with a thickness of 0.04 mm. The electrode thickness is 0.008 to 0.010 mm, while the distance between the two electrodes is 0.06 to 0.08 mm. From these dimensions, it is evident that we are far from ideal parallel-plate capacitor geometry, but we are able to detect capacitance changes associated with phase transitions. With this arrangement, we also detected conductivity changes in other samples having semiconductor-to-metal transitions.

There is a 1-mm-diam hole at the center of the base, so none of the base material is in the region of contact of the lower diamond anvil and the two electrodes. This minimizes sliding of the electrodes out of the central region, and avoids intrusion of base material into the capacitor region during compression. The electrodes and lead-in wires were fixed on a Plexiglas insulating mount and connected by conductive glue, as seen in Fig. 1(b).

The central pressures in the samples were calculated by the Hertz formula

$$p_0 = 3\langle p\rangle/2 = 3F/2S, \tag{2}$$

where p_0 is the central pressure, and $\langle p\rangle$ is the average pressure, as determined by the applied force F and diamond face area S. These opposing faces are regular 16-sided polygons with 0.5 mm diameter.

The samples were obtained by grinding to a fine powder single crystals which were grown by evaporation from an aqueous solution. Preparation for a measurement involved placing a small quantity of the powdered sample at the center of the electrode pair, which had been previously centered on the lower diamond anvil [Fig. 1(b)]. It was not possible to control the quantity of sample trapped between the diamond anvils and located between the electrodes. This accounts, in part, for the variation in capacitance observed from sample to sample.

Water adsorbed by the powder samples affected the measured capacitance. In the earlier measurements, no precaution was taken to preclude adsorption of water. Several were studied after drying in a desiccator for three or more weeks, but with no provision for maintaining the apparatus free from water vapor during measurements. Fi-
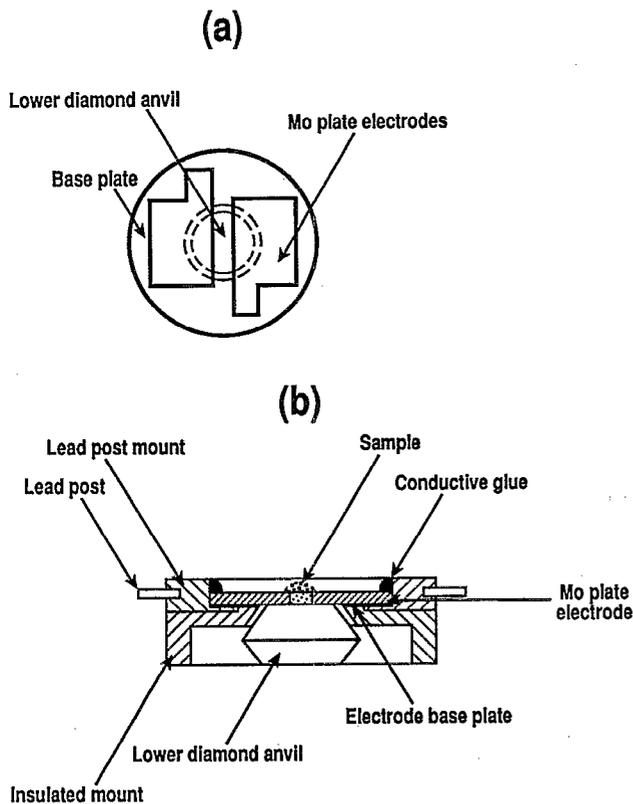
(a)

(b)

FIG. 1. (a) Top view of Mo electrodes placed on the lower diamond anvil. (b) Cross sectional view of the Mo electrodes, electrode holder, and leads in place on the lower diamond anvil.

nally, samples were studied that had been dried for at least one month, and dry argon was passed through the cell during the experiment. Also, during the period between the first and second compression, the entire DAC was held in a dry argon environment.

All of the capacitance measurements were made with a General Radio Model 1621 Capacitance Measurement System, operated at 500 Hz. Each of the samples studied was prepressed. Then, following a suitable interval, it was compressed to near 14 GPa, with capacitance measurements made at static pressures at pressure intervals of a few tenths of a GPa. The pressure was then reduced to one atmosphere and the sample, undisturbed in the DAC, was allowed to relax for a period ranging from 24 to 72 h. A second compression was then accomplished.

III. EXPERIMENTAL RESULTS

A. KH$_2$PO$_4$

The capacitance-pressure relationship for 16 KDP samples was measured at room temperature to about 14 GPa in the present work. Eleven of the samples were not dry, the remaining five were dry. Argon was passed over the dry samples during measurement.

Figure 2 shows the C-p (capacitance-pressure) relationship for one of the non-dry samples for its first compression. Its capacitance gradually changes up to 2.5 GPa, where it changes suddenly. In addition, the slope of the C-p
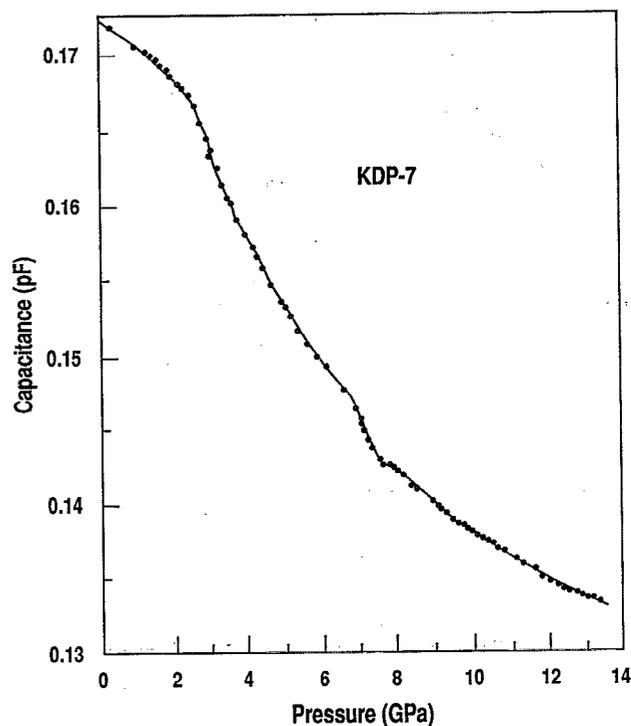

FIG. 2. C-p relationship for a KH$_2$PO$_4$ sample from the first compression to 14 GPa. The sample was not dried, and not maintained in a dry argon atmosphere during the measurement. The sample was compressed to 2.6 GPa prior to the measurement.

curve suddenly increases at about 7.0 GPa. These phenomena can be seen more clearly in results for other samples shown in Figs. 3–5. Figures 3 and 4 show the C-p relations for the two dry samples during their first compressions to high pressure, which was done under an argon atmosphere. These two samples were prepressed to 2.5 and 5.2 GPa, respectively, before the measurements. Figure 5 shows the
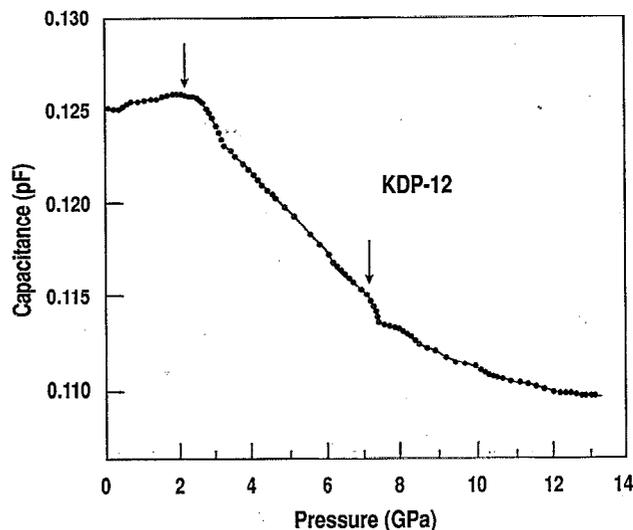

FIG. 3. C-p relationship for a dry KH$_2$PO$_4$ sample from the first compression to 14 GPa. The sample was precompressed to 2.6 GPa and maintained in a dry argon atmosphere during the measurement.
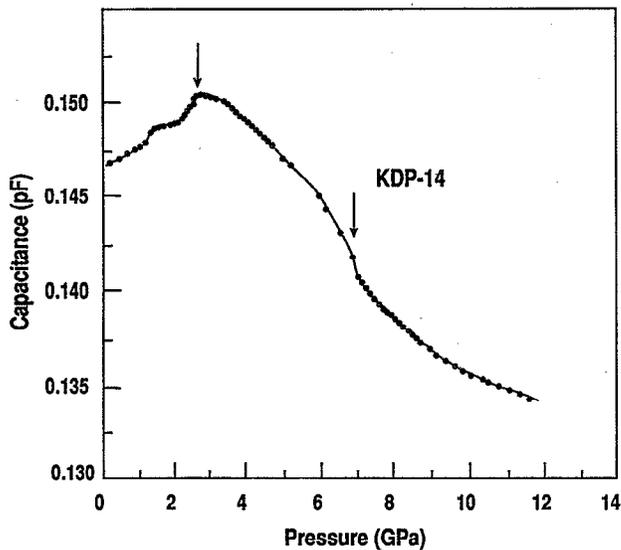
FIG. 4. C-p relationship for a dry KH_2PO_4 sample from the first compression to 14 GPa. The sample was precompressed to 5.2 GPa and maintained in a dry argon atmosphere during the measurement.

C-p relation for the non-dry sample for its second compression. These figures show that the slopes of the C-p curves change suddenly, near both 2.5 and 7.0 GPa. In particular, the capacitance gradually increases up to 2.5 GPa, and suddenly decreases above 2.5 GPa.

These phenomena were also observed repeatedly in other samples. We think that the sudden slope change in the C-p curves is indicative of a phase transition. Therefore, we think that there are two phase transitions in KH_2PO_4 at room temperature below 14 GPa, namely at 2.5 and 7.0 GPa.
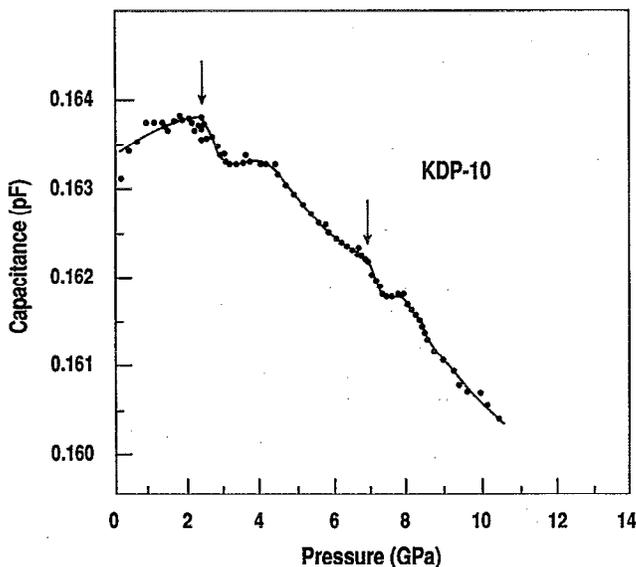

FIG. 5. C-p relationship for a KH_2PO_4 sample from the second compression to 14 GPa. The sample was not dried and not maintained in an argon atmosphere during the measurement.
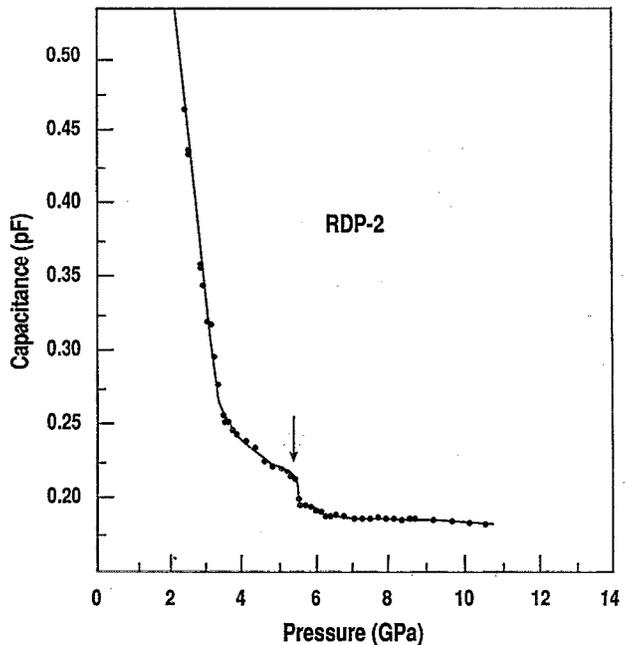

FIG. 6. C-p relationship for a RbH_2PO_4 from the first compression to 14 GPa. The sample was not dried, not maintained in an argon atmosphere during the measurement, and was precompressed to 0.7 GPa.

B. RbH₂PO₄

The C-p relations for 11 RDP samples were measured at room temperature for pressures up to about 14 GPa. Six of these samples were not dry, the other five were dry. Argon was passed over the dry samples, and over some non-dry samples, during high-pressure measurement.

Figure 6 shows the C-p relation for one of the non-dry samples that had been prepressed to 0.7 GPa. No argon was passed over this sample during measurement. Figures 7 and 8 show the C-p relation for two of the dry samples. No argon was used during the measurement of the Fig. 7 sample, but argon was passed over the Fig. 8 sample during measurement. We see in Figs. 6–8 a sudden change in the C-p curves near 5.4 GPa. This sudden change was also observed in other samples. We believe this shows that RbH_2PO_4 has one phase transition at room temperature below 14 GPa, at 5.4 GPa.

IV. DISCUSSION

A. Phase transition in RbH₂PO₄

From high-pressure infrared data[2] and the p-T phase diagram[4] for RDP, which is reproduced in Fig. 9 with our room-temperature point added, it appears that the transition observed in our experiments is the same as that seen by Blinc and co-workers.[2] This transition is from the paraelectric tetragonal phase III to a high-pressure phase V. From the infrared spectra, it was inferred[2] that, in phase V, the PO_4 tetrahedra are distorted and the protons are ordered, but the structure of this phase has not been determined.
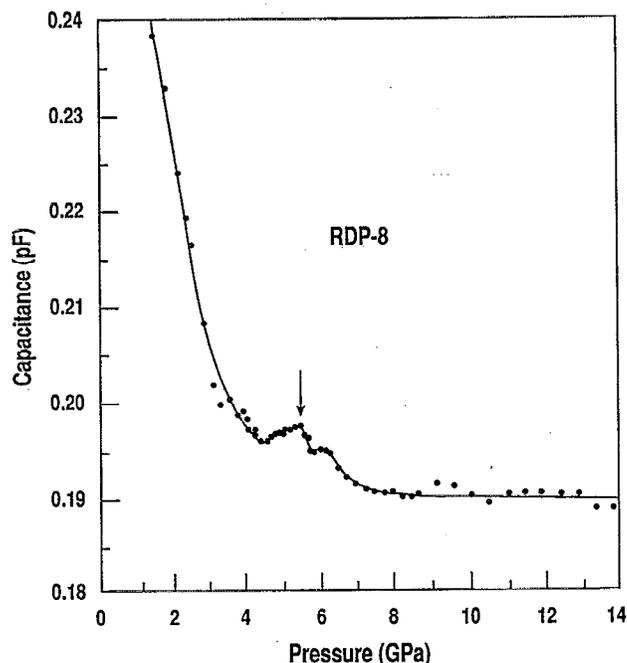
FIG. 7. C-p relationship for a dry RbH_2PO_4 sample from the second compression to 14 GPa. This sample was not maintained in an argon atmosphere during the measurement.

B. Phase transitions in KH_2PO_4

According to the p-T (pressure-temperature) phase diagram of KDP,[3] reproduced in Fig. 10 with our room-temperature points added, the first room-temperature phase transition with increasing pressure is probably from the paraelectric tetragonal phase II to phase II″ (called phase IV in Ref. 3, but not to be confused with the RDP
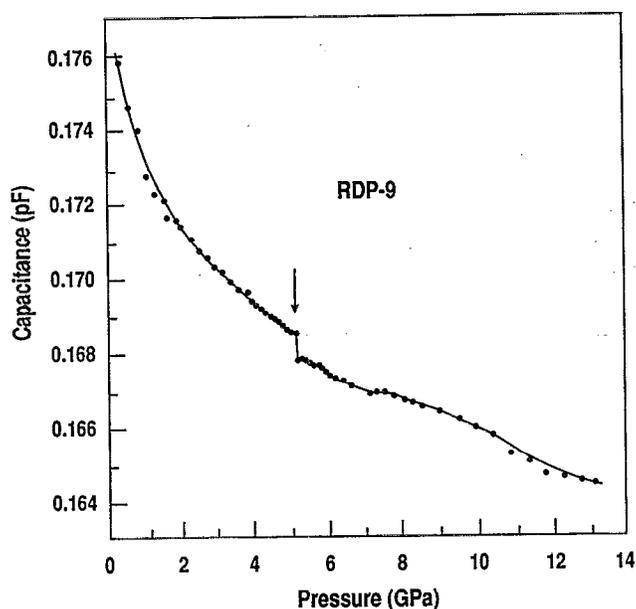
FIG. 8. C-p relationship for a dry RbH_2PO_4 sample from the second compression to 14 GPa. This sample was maintained in an argon atmosphere during the measurement.

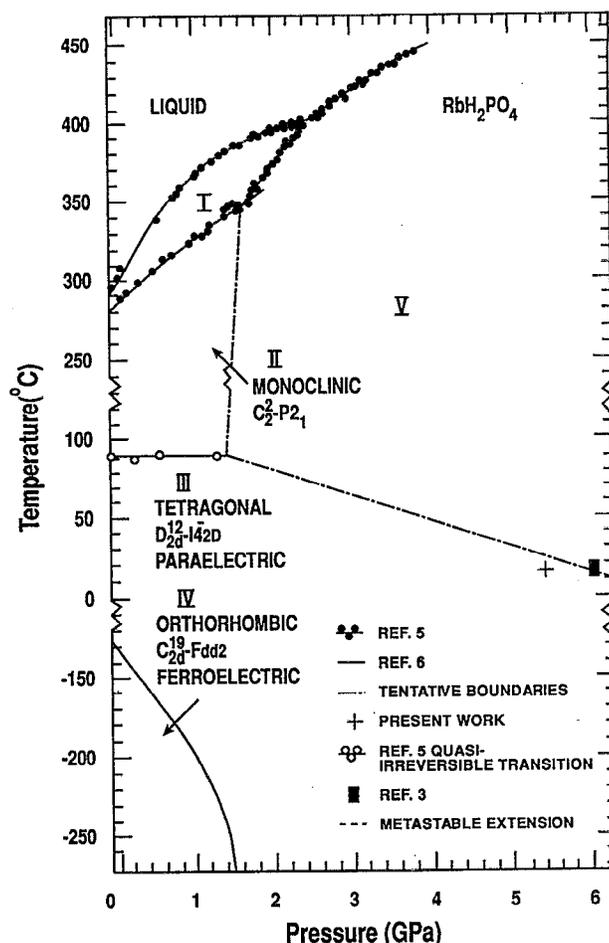FIG. 9. Results of the present work shown on the phase diagram of RbH_2PO_4 from Ref. 4.

ferroelectric phase called phase IV in Fig. 9 and Ref. 4). Phase II″ may correspond to the monoclinic phase II in RDP shown in Fig. 9, but it is also possible that phase II′ corresponds to phase II.[4] The second room-temperature transition is probably from phase II″ to another high-pressure phase V whose structure is not yet known. Phase V is most likely analogous to phase V in RDP. The need is obvious for additional points in the 50 to 200 °C range to verify these room-temperature phase boundary assignments. We are planning modifications to our DAC apparatus to allow operation at these temperatures.

C. Sources of error in this measurement method

Two sources of error in the measurement of pressure were identified. Ideally, the electrodes and sample material between them should be centered between the anvils. Deviations from ideal centering may explain small differences from sample to sample in the apparent pressures, at which significant C vs p slope changes occur that indicate phase transitions. Also, a systematic error may arise from the very large radial pressure gradient that occurs in an ungasketed DAC, as was used in this work. The resulting shear stress causes the measured transition pressure under such nonhydrostatic conditions to be lower than under hydro-
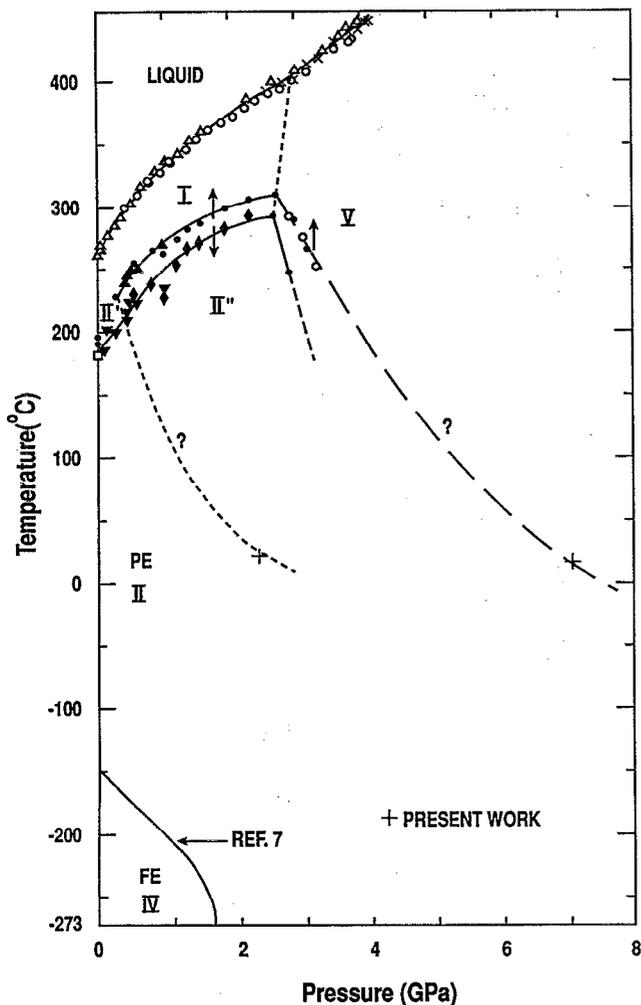
FIG. 10. Results of the present work shown on the phase diagram of KH_2PO_4 due to Rapaport (see Ref. 3), and to Samara (see Ref. 7).

static conditions. This may explain why our transition pressure of about 5.4 GPa for RDP is lower than the 6 GPa value reported by Blinc and co-workers.[2]

The process of balancing the capacitance bridge provides a conductance value for the sample and cell as well as the capacitance value. Plots of conductance versus pressure show little change at the transition pressures. Conductance is strongly affected by the presence of adsorbed water in the sample and on the surfaces of the electrode base and holder material.

Adsorbed water alters the value of the measured capacitance. This has no serious effect on our ability to locate the transition by observing capacitance change, if the adsorbed water content remains constant. However, the capacitance of a dry sample in room air at constant pressure showed a steady drift in capacitance and conductance as it adsorbed water from the air. This drift was eliminated by passing dry argon gas through the cell during the experiment.

D. Prepressing of samples

All of our samples were prepressed to definite pressures before the measurements. Our experience showed

that prepressing is important for obtaining good experimental results. The purposes of prepressing are to eliminate the gaps between the powder grains, and to give the electrodes part of their final deformation before the measurement.

The electrodes have a certain initial thickness, which will decrease under pressure, thus affecting the capacitance measurement. Prepressing in a suitable pressure range is important to minimize electrode deformation during measurement. If the prepressing pressure is too high, the electrodes may break. From Figs. 3–4, showing C-p plots for dry KDP after prepressing to 2.6 and 5.2 GPa, respectively, we see that the first phase transition is more obvious, and we expect that the measured C-p relation is closer to the correct one.

V. CONCLUSIONS

The experimental results for KDP and RDP show that our measurement method is feasible and reliable, i.e., phase transitions in insulators at high pressure can be detected by measuring capacitance change. However, because of electrode deformation and poorly known electrode-sample geometry, the dielectric permittivity at high pressure cannot be precisely measured. Improvements planned in the measurement method may allow measurement of dielectric permittivity with greater accuracy.

Our conductance results for KDP and RDP show no obvious changes in conductance at the transition pressures. Thus, it is very difficult to detect nonmetallic transitions in insulators at high pressure by measuring conductance change. Our diamond anvil cell capacitance method is superior for finding such high-pressure insulator-to-insulator transitions, especially if they are accompanied by large dielectric anomalies as is common for many such transitions.

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